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A Crystal-Structural Comparison of Polyethylene with *n*-Paraffins: I. Effects of the Crystal Surface on the Crystalline Core

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A light was thrown upon the crystalline structure of polyethylene from a study on the *n*-paraffins which were both chemically and crystallographically analogous to polyethylene. The (200)_s spacing increased to various extents as a result of the phase transition of *n*-C₃₆H₇₄ (from the monoclinic M₀₁₁ crystal to the orthorhombic) or the formation of the mixed crystal of two different *n*-paraffins in chain length, *i.e.* *n*-C₃₂H₆₆ and *n*-C₃₅H₇₂. This spacing increase was caused by the methyl end groups which change their manner of packing at the crystal surface. The smaller lattice spacings were observed in the as-grown polyethylene crystal with larger thickness. Although the thickness of solution-grown crystal was increased by annealing, the spacing increased when the thickness of annealed crystal ranged from 180 Å to 220 Å. The thickness dependence of the lattice spacing in polyethylene was discussed on the basis of two types of effects; (i) a conformational strain to be stored in a fold at the lamellar surface and (ii) the interactions between bulky folds.

INTRODUCTION

Since it was found that polymer crystals grown in the form of lamella are composed of folded chains, the molecular conformation of folded part,¹⁻⁵⁾ the packing manner of folds at the lamellar surface⁶⁻⁷⁾ and the other structures and properties related with the chain folding have been studied repeatedly.^{2,8)}

The cell dimensions of a polyethylene crystal largely depend on the thermal history⁹⁾ as well as the crystallization conditions such as temperature or whether crystals are grown from melts or solutions.¹⁰⁻¹¹⁾ The as-grown crystals of larger thickness (obtained from melts or from solutions at higher temperatures) have a smaller unit cell. The more shrunk cells are observed for longer paraffins which form thicker platelets,¹²⁾ and thus the cell dimensions depend on the chain length. The dependence of the cell dimensions on the thickness of lamella or platelet results from the effects of the structure of lamella surface upon that of crystalline core.

Despite the difference in chain length, polyethylene and paraffins are constituted of the same chemical repeating unit -CH₂- and crystallize in the form of lamella or platelet with the same subcell.¹³⁻¹⁸⁾ Since *n*-paraffins have the chemically and crystallographically defined structure, they have been utilized as the model substances for the study on the behavior of the intensity of small angle scattering peak,¹⁹⁻²¹⁾ the effect of the crystal surface on the crystalline core,¹²⁾ the morphology,²²⁾ and the mechanical property²³⁾ of polyethylene crystals. However, the basal surface of

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paraffin platelet is composed of methyl end groups and the surface is composed of folds consisting of several segments in the case of polyethylene lamella. On the basis of the observed change in cell dimensions with the phase transition of *n*-C₃₆H₇₄ crystal and with the formation of mixed crystals of *n*-C₃₂H₆₆ and *n*-C₃₅H₇₂, the surface effects on the crystalline core are discussed, and the effect of the chain folding in polyethylene crystal on the crystal lattice is also referred in the present paper.

EXPERIMENTAL

Three *n*-paraffins, *n*-dotriacontane *n*-C₃₂H₆₆ (m.p. 342.5°K) *n*-pentatriacontane *n*-C₃₅H₇₂ (m.p. 347.4°K²⁴) and *n*-hexatriacontane *n*-C₃₆H₇₄ (m.p. 349.1°K²⁵), were used. As polyethylene sample, an unfractionated linear polyethylene Sholex 6050 produced by Showa Denko K.K. was used. The paraffins were crystallized from a 0.5 wt% solution in *n*-heptane at about 277°K by keeping it in a refrigerator. The platelets thus grown were slowly filtered off at that temperature and the oriented mat, in which platelets were parallelly arranged with respect to the mat surface, was prepared. The mat was dried in vacuum for 24 hrs at room temperature.

Polyethylen single crystals were isothermally grown from a 0.05 wt% solution in *p*-xylene. The oriented mats were prepared by sedimentation. The mats were annealed for 24 hrs in nitrogen atmosphere in a temperature range from 373 to 398°K. For further comparison of the structure of crystals obtained under different conditions, polyethylene was also crystallized isothermally from the melts at various temperatures (the highest temperature was 402°K) or by quenching the melts in liquid nitrogen.

The wide and small angle X-ray diffraction measurements were made with a Shimadzu X-ray diffraction apparatus VD-1 using Ni-filtered copper radiation. For the measurements at higher temperatures, samples were kept in an aluminium holder held in a small chamber with Mylar window. Temperature control was performed by circulating a temperature-controlled liquid around the chamber. The liquid used for cooling below room temperature was a system of dry ice-methanol and that for heating above room temperature was a mixture of water and ethylene glycol. The temperature was measured with a thermocouple put on a sample surface and could be maintained within 0.5°C during the measurement. The small angle X-ray measurement of very long periods was photographically made with pinhole collimation and Ni-filtered copper radiation from a rotating anode X-ray source, Rigaku Denki Rotaunit RU-3H.

POLYMORPHISM AND UNIT CELL

n-Paraffins exhibit polymorphism. The modification which appears in a paraffin crystal depends on the chain length of paraffin and the crystallization condition. The orthorhombic, several kinds of monoclinic, triclinic and hexagonal forms have been found. The crystal structure of each form has been analyzed in detail on selected paraffins; the orthorhombic form of C₂₃¹⁷⁾ and C₃₆,¹⁴⁾ the monoclinic form of C₃₆¹⁵⁾ and the triclinic form of C₁₈.²⁶⁻²⁷⁾ (C₁₈, C₂₃, and C₃₆ are used as the abbreviations

of $n\text{-C}_{18}\text{H}_{38}$, $n\text{-C}_{23}\text{H}_{48}$ and $n\text{-C}_{36}\text{H}_{74}$, respectively.) The unit cells of the orthorhombic and monoclinic forms studied here are schematically shown in Fig. 1. The subcell in Fig. 1 corresponds to the usual unit cell of polyethylene crystal.¹³⁾

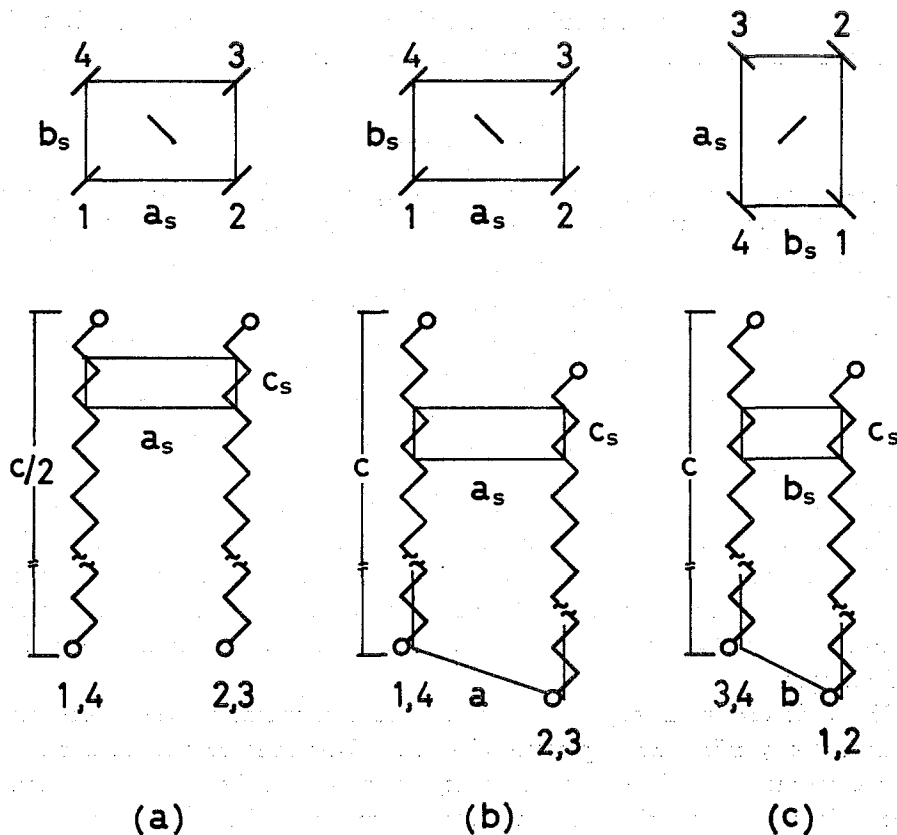


Fig. 1. Subcell and chain projections in various modifications of paraffins. a_s , b_s , and c_s are the cell dimensions of subcell. c is the cell dimension of the following macrocells. (a) orthorhombic macrocell. The cell dimensions a and b are equal to a_s and b_s , respectively. (b) monoclinic M_{101} macrocell. The cell dimension b is equal to b_s . (c) monoclinic M_{011} macrocell. The cell dimension a is equal to a_s .

The triclinic form appears in the stable state of even-numbered paraffins shorter than C_{26} at a temperature far below the melting temperature. The monoclinic forms are classified into two kinds. The first kind of the form is formed from the orthorhombic unit cell by staggering successively the adjacent molecules along the b -axis by some $-\text{CH}_2-$ units in a direction parallel to the c -axis — M_{0kl}^* , and the second kind by staggering the adjacent molecules along the a -axis by some $-\text{CH}_2-$ units in the same direction — M_{h0l}^* . The degree of staggering is not fixed but depends on the crystallization condition. The monoclinic form of C_{36} corresponds to M_{011}

* The notation is used according to Sullivan and Weeks.¹⁹⁾ The triplets $0kl$ and $h0l$ denote the Miller indices which refer to the subcell lattice plane parallel to the plane in which methyl end groups are packed.

in which molecules are staggered by four $-\text{CH}_2-$ units. Even paraffins longer than C_{28} crystallize in the orthorhombic and monoclinic forms. The type of the resulted form depends largely on the crystallization condition. All odd-numbered paraffins crystallize in the orthorhombic form by gentle solution crystallization. However, the M_{h01} type of monoclinic modification appears on solidification under a drastic condition such as quenching of the paraffin melt. Most of even and odd paraffins exhibit the hexagonal form (called the rotator phase) at a temperature just below the melting temperature. Thus the crystal form depends only on the chain length, and we may conclude that the steric interactions between the bulky end groups arranged at the platelet surface have the considerable influence on the packing of paraffin chains.²⁸⁻²⁹⁾

RESULTS AND DISCUSSION

Figure 2 shows a series of X-ray diffraction photographs of C_{36} taken at various temperatures. The modification of as-grown crystal was identified as the monoclinic M_{011} form from the measurement of (001) spacing. In Fig. 2a, the 020_s reflection splits into two arcs apart from the equator, while the $00l$ and 200_s reflections remain on the meridian and equator, respectively (The suffix *s* denotes the subcell). Since the platelet surface corresponding to the basal plane of unit cell is parallel to the surface of mat, this orientation of arcs is uniquely explained on the basis of the unit cell of M_{011} . With increasing temperature, the 020_s reflections converge suddenly on a single arc at about 338°K , while the orientation of $00l$ and 200_s reflections remain unchanged (see Fig. 2c). The change in the diffraction pattern shows that the phase transition from the monoclinic M_{011} form to orthorhombic one occurs. From the viewpoint of the molecular orientation in a platelet, this phase transition is interpreted as follows; paraffin chains which tilt to the platelet surface in original crystal stand perpendicularly to the surface by sliding on the $(010)_s$ plane in the **c**-axis direction. The orthorhombic form transforms to hexagonal one with the further increase of temperature and eventually crystals melt. Another monoclinic form whose structure is not defined appears clearly in the process of the transformation to the hexagonal form. The split of 200_s arc in Fig. 2d shows that the chains situated along the **a**-axis are successively displaced with respect to adjacent one in the **c**-axis direction so that the angle between **a**- and **c**-axes differs from 90° . The form may be assigned to M_{101} by the measurement of the splitting angle of arc. When crystals were cooled to room temperature after the phase transition of the monoclinic M_{011} to the orthorhombic form had been completed, the crystal form did not return to the original monoclinic form but remained orthorhombic. Namely this transition was irreversible. No phase transition was observed in the second and further cycles. The (001) spacing jumped suddenly at about 338°K from 42.5 \AA to 48.1 \AA which corresponds to the (001) spacing of orthorhombic form. Thus the phase transition was confirmed from the change in (001) spacing.

Figure 3 shows the change of $(200)_s$ and $(020)_s$ spacings of C_{35} and C_{36} with temperature. The $(200)_s$ spacing of the starting monoclinic crystal increases monotonically with temperature, jumps suddenly by 0.02 \AA at about 338°K where the phase

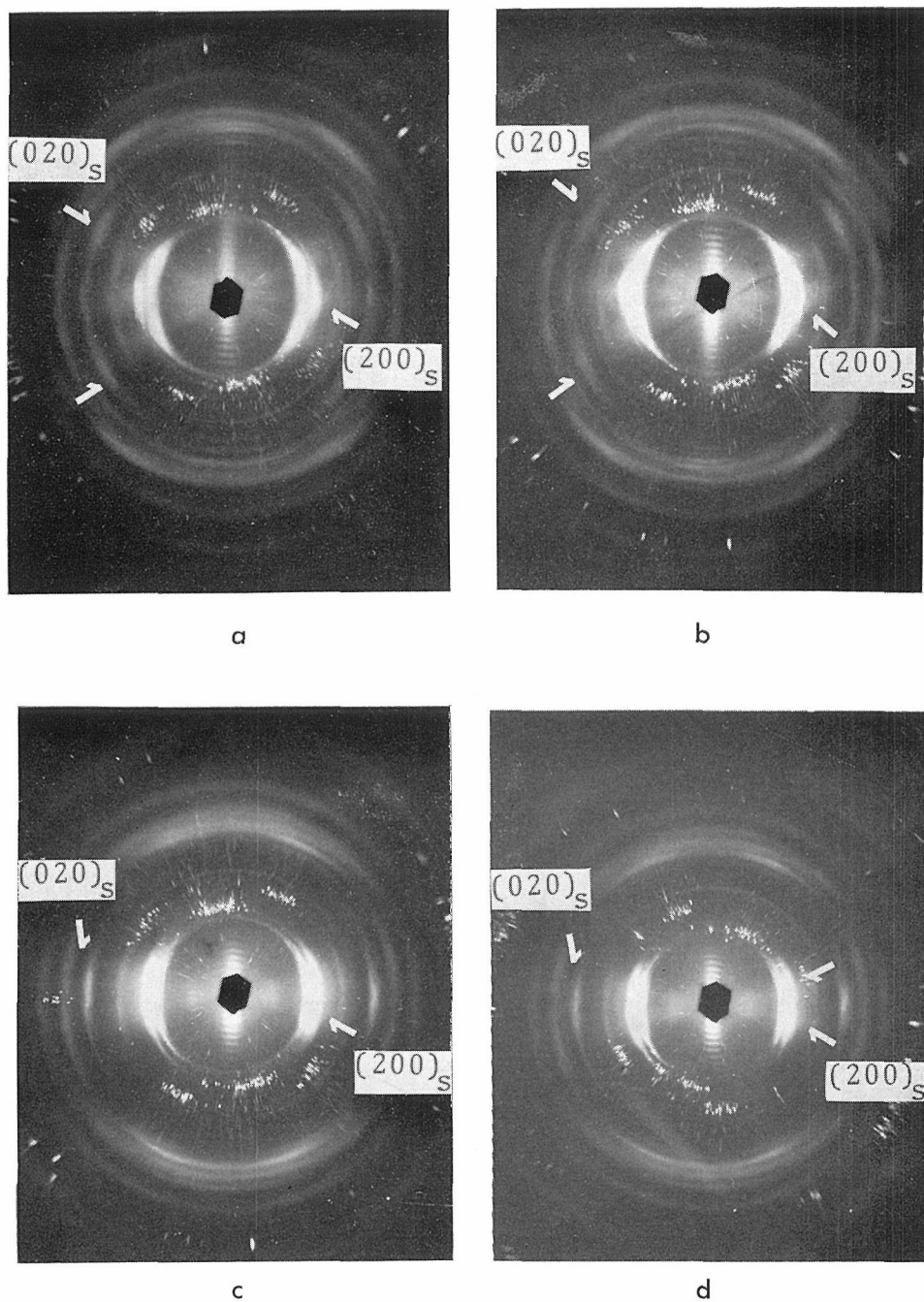


Fig. 2. X-ray diffraction photographs of C_{36} crystal taken at (a) room temperature, (b) 333°K , (c) 339°K , and (d) 345°K . The mat of platelets was set in such a way that the normal to the surface of mat was vertical in these photographs and that the incident direction of X-ray beam was parallel to the surface. The spotty contamination seen in the photographs is due to the diffraction of aluminium foil used for the window of the high temperature chamber keeping the samples in it.

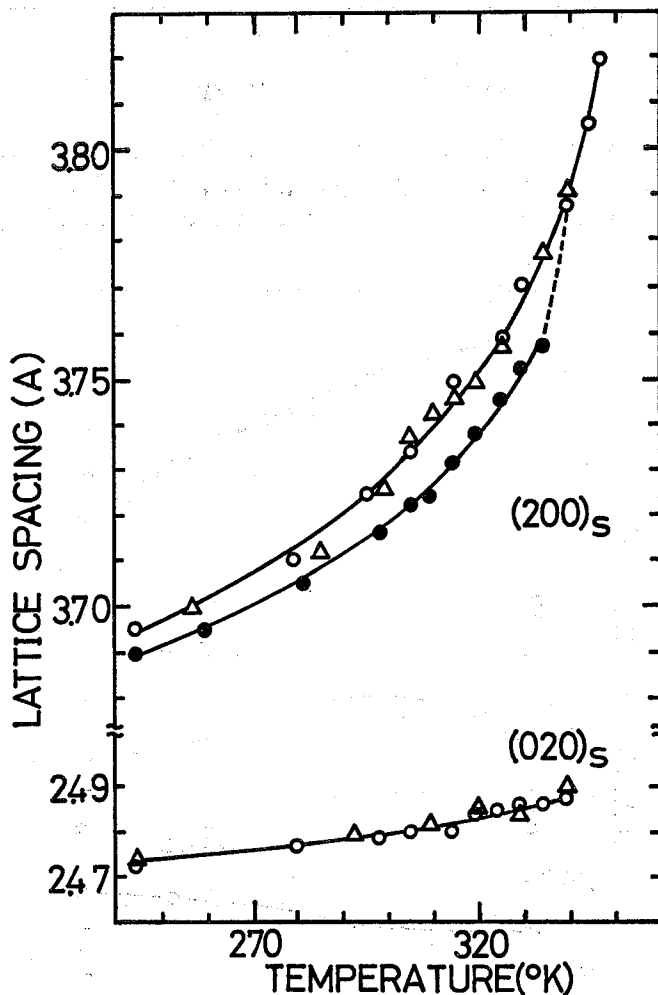


Fig. 3. The $(200)_s$ and $(020)_s$ spacings of C_{35} and C_{36} crystals as a function of temperature. Filled circles (●) denote the lattice spacing of monoclinic M_{011} crystal of C_{36} while open circles (○) that of the orthorhombic crystal. Triangles (Δ) shows the lattice spacing of C_{35} crystal.

transition occurs and again increases remarkably till the crystal melts. When the crystal is cooled down after the phase transition to the orthorhombic form is completed, the $(200)_s$ spacing does not return to the original value but expands by 0.01 \AA at room temperature. In the second cycle, the lattice spacing changes reversibly with temperature along the upper line in Fig. 3. The phase transition of M_{011} to the orthorhombic form results in the increase of $(200)_s$ spacing. The $(200)_s$ and $(020)_s$ spacings of C_{35} crystals change also reversibly with temperature and their values are in good agreement with those of orthorhombic C_{36} . The chain length of C_{36} is 1.27 \AA longer than that of C_{35} . Such small difference in chain length has no effect on the lattice spacing when the crystal form is the same. Methyl end groups at the surface of the monoclinic platelet are successively displaced with respect to the adjacent group

in a direction parallel to the *c*-axis and those of the orthorhombic crystal lie in the plane at right angle to the *c*-axis (see Fig. 1). This change of the packing manner of methyl end groups at the platelet surface affects the intermolecular distance of paraffin chain in crystal.

The binary mixtures of C_{32} and C_{35} with various mixing ratio were crystallized from the solution. Figure 4 shows the $(200)_s$, $(020)_s$, and (001) spacings of the crystal of the binary mixtures as a function of the molar fraction of C_{32} component.

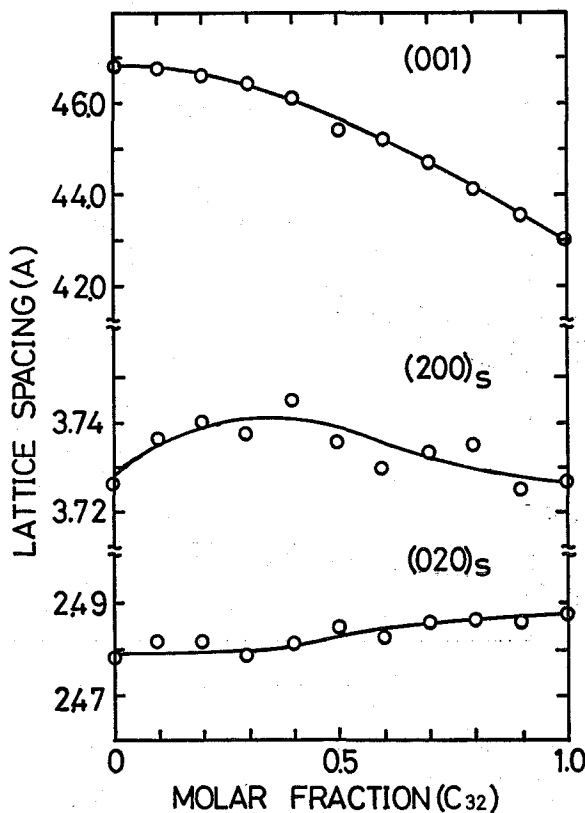


Fig. 4. The (001) , $(200)_s$, and $(020)_s$ spacings of mixed crystal of C_{32} and C_{35} paraffins as a function of the molar fraction of C_{32} component. The spacings were determined at room temperature.

The (001) spacing decreases continuously from the value of pure C_{35} to that of pure C_{32} with the increase of the molar fraction of C_{32} . If either species of the two paraffins swarms and crystallizes separately, the (001) spacing belonging to either crystal should be observed. The continuous decrease of the (001) spacing proves that the mixed crystals are formed so that C_{32} is incorporated in the crystal of C_{35} in the low concentration of C_{32} and *vice versa* in the high concentration.³⁰ When the molar fraction of C_{32} is between 0.3 and 0.5, the $(200)_s$ spacing becomes maximum and 0.01 Å larger than those of pure paraffins. The $(020)_s$ spacing increases from 2.48 Å of pure C_{35} to 2.49 Å of pure C_{32} in the range of the fraction from 0.4 to 0.6. The difference

of chain length between two paraffins is about 3.8 Å and produces the irregular packing of methyl end groups within the domain of platelet at the depth from the surface to over 3.8 Å. The roughness of platelet surface due to the irregular packing of methyl end groups may cause the expansion of (200)_s spacing and the change in (020)_s spacing.

The steric interaction of methyl end groups at the surface of platelet affects the crystalline core as seen from the above results of the phase transition of C₃₆ and the formation of mixed crystal. The surface effect is expected to be less for longer paraffins. Davis *et al.*¹²⁾ have found out from the precise measurement of lattice spacings of various paraffins that the lattice spacing decrease in proportion to the reciprocal of the thickness of platelet. They have pointed out that the dependence of lattice spacing on the platelet thickness was due to the steric interaction at the surface and also arose (although indirectly) from the effects of the surface on the thermal vibration of molecular chains. The latter thermal effect may be more eminent for shorter chains. As the difference of chain length was as small as 3.8 Å or zero in the present work, the observed change in lattice spacings arose directly from the steric interactions at the surface rather than from the indirect effect of the

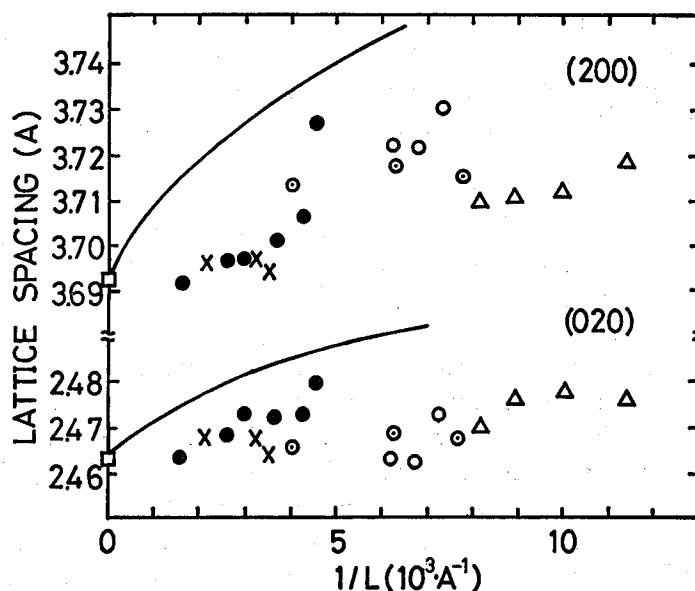


Fig. 5. The (200) and (020) spacings of various polyethylene crystals as a function of the reciprocal of long period L . All measurements were made at 293°K.

△; as-crystallized from the solution at various temperatures (77°K–358°K).

●; as-crystallized from the melts at various temperatures (77°K–402°K).

○; crystallized from the solution by quenching it to 77°K and annealed at various temperatures.

⊙; crystallized isothermally from the solution at 353°K and annealed at various temperatures.

x; crystallized from the melt by quenching it to 77°K and annealed.

□; crystallized at 5000 atm. and 593°K.

The solid lines show the (200) and (020) spacings which are calculated by Eq. (1).

surface on the thermal motions.

The lattice spacings of polyethylene crystals depend on the formation process; the solution- and melt-crystallization, annealing *etc.*⁹⁻¹²⁾ The (200) and (020) spacings of polyethylene crystals which were prepared on various conditions are shown in Fig. 5 as a function of the reciprocal of the long period. The lamellar thickness of polyethylene crystal prepared by quenching the melts in liquid nitrogen was about 250 Å and smallest among the melt-crystallized polyethylenes (though the present work, the lamellar thickness was assumed to be equal to the long period). The lamellar thickness of single crystal was about 180 Å at the thickest. The crystals of the thickness between these two values were prepared by annealing thin crystals grown from the solution. The polyethylene crystallized at 5000 atm. and 493°K was used as a crystal of the extremely large thickness.

As seen from Fig. 5, the (200) and (020) spacings of as-grown crystals decrease with the increase of lamellar thickness, but the thickness dependence of the lattice spacings is different between the melt- and solution-grown crystals. The (200) spacing of annealed single crystals does not always decrease with the increase of lamellar thickness but increases when the thickness ranges from 180 Å to 220 Å. This result suggests that the annealed single crystals do not take the same physical state as the as-grown ones of the same thickness.

The decrease of lattice spacings with the increase of the lamellar thickness has been explained by Davis *et al.*¹²⁾ in terms of such surface effects as discussed in the case of paraffins. Although polyethylene and paraffin crystallize in the form of lamella or platelet, polyethylene crystals are distinguished from those of paraffins in respect to the following point: polyethylenes fold back and forth many times in a lamella, while paraffins extend. In other words, the surface of polyethylene lamella consists of folds instead of the methyl end groups of paraffin crystal. Folds are more bulky than the methyl end groups so that they pronouncedly exert an influence of their steric interaction at the surface upon the core of lamella to expand the lattice dimension. In the case of polyethylene crystals composed of such folds, two kinds of surface effects must be taken into account; (1) the conformational strain of folded part by folding of molecular chain at the surface and (2) the steric hindrance between folds which refer to the methyl end groups. Several conformational analyses of fold succeeding to Frank's first proposition show that on folding back at the lamellar surface the polyethylene chain cannot accomodate itself to the adjacent lattice point only by the conformational change with transforming trans bonds into *gauche* ones. Chain folding will inevitably accompany distortions in the bond angle and bond length of folded chain segments. The excess strain energy due to this conformational distortion should be added as the additional surface energy to the increase of energy due to the bond transformation of trans to *gauche*. The conformational distortion of folds propagates possibly to the core of lamella to expand and distort the lattice. Newman and Kay³¹⁾ have estimated the excess strain energy at $\sim 20 \times 10^{-14}$ erg/fold on the basis of the conformation of folded part of cyclic paraffin. Now let us estimate how the cell dimensions expand due to the strain of folds. The assumptions are set as follows; (1) the molecules behave themselves like a rigid body and (2) the strain energy is equally shared between two parts to expand the cell in the **a**- and **b**-axes, respectively.

When a column of cross-section $\mathbf{a} \cdot \mathbf{b}$ and height L is expanded by $\Delta \mathbf{a}$ and $\Delta \mathbf{b}$ in the \mathbf{a} - and \mathbf{b} -axes, respectively, the increase of lattice energy is expressed by

$$U = \frac{1}{2} \left[E_a \left(\frac{\Delta \mathbf{a}}{\mathbf{a}} \right)^2 + E_b \left(\frac{\Delta \mathbf{b}}{\mathbf{b}} \right)^2 \right] \mathbf{a} \mathbf{b} L \quad (1)$$

where E_a and E_b denote Young's moduli in the \mathbf{a} - and \mathbf{b} -axes, \mathbf{a} and \mathbf{b} the cell dimensions and L the lamellar thickness, respectively. When the crystal is at equilibrium, U is equal to the excess strain energy. By putting the values of $\sim 3 \times 10^{11}$ dyne/cm² for E_a and $\sim 6 \times 10^{11}$ dyne/cm² for E_b ,³¹⁾ in Eq. (1), the expansion of (200) and (020) spacings is calculated and shown in Fig. 5 with the solid curve against the reciprocal of lamellar thickness.

The surface free energy amounts to 100 erg/cm² by adding the excess strain energy to the increase of energy due to the conformational change of trans bonds to *gauche* ones in the folded part. The values of surface free energy obtained by various theories on crystallization, melting and thickening of lamella by annealing range from 30 erg/cm² to 140 erg/cm². The present value is rather large. When a smaller value is used in the calculation, the expansion of cell dimensions is to be reduced. The energy calculations on the conformation of folded part³⁻⁵⁾ predict that the excess strain energy may be relaxed by the increase of the segment number of folded part without distorting bond angles and bond lengths or by distorting the conformation of some tens carbons of stem segments just below the surface, and the infrared spectroscopic observation by Tatsumi and Krimm³³⁾ shows that the plane in which polyethylenes are folded back and forth on themselves is different between melt- and solution-grown lamellae. Thus as the chain folding itself is complicated and not made clear, the above consideration is over-simplified. However, the above estimation shows the possibility that the lattice spacing expands due to the conformational strain of fold. Various modes of deformation of a single crystal such as twinning, pleat, corrugation *etc.* are discussed in terms of the anisotropic surface stress due mainly to this intrafold interaction.³⁴⁾

To relax the steric stress of folds at the lamellar surface, folds are arranged in a staggered configuration in such a manner that the fold surface is inclined to the \mathbf{c} -axis direction. This staggering results in the hollow pyramid of single crystal and its related crystal habits.⁶⁾ The molecular angle of tilt is found to be about 60° by means of the electron diffraction and electron microscopy. Niegish and Swan³⁵⁾ have looked at the hollow pyramidal habit from the crystallographic point of view and proposed the triclinic macrocell in which the cell dimension \mathbf{c} is equal to the fold length and tilts to the basal plane just as in the case of monoclinic and triclinic macrocell of paraffin. Thus the molecular orientation and arrangement in polyethylene lamella may be compared to that of paraffin crystal, and the steric interaction between folds may be considered from the same viewpoint as for the case of methyl end groups of paraffins. The dependence of lattice spacings of polyethylene lamella on its thickness may arise from the steric interaction between folds as well as the anisotropic stress due to the chain folding.

When single crystals are annealed, folds which are staggered more or less regularly at the lamellar surface are rearranged through the partial melting.³⁶⁾ The rearrange-

ment of folds will accompany a change in the degree of staggering and consequently the molecular inclination to the lamellar surface will vary. When folds are packed in the surface regularly before and after annealing, this change in molecular arrangement may be regarded as "a sort of phase transition" in comparison to the phase transition of C_{36} according to the proposition by Niegish and Swan. Since real annealing hardly reaches such a thermodynamic equilibrium as crystallization from a solution, however, mismatch and irregular staggering of folds may arise from the nonuniform fold length and the large steric hindrance of fold *etc.*, and may make the fold surface more rough. Such a lamellar surface of annealed single crystal may be compared to that of mixed crystals of C_{32} and C_{35} . As various kinds of defects are introduced into crystals by annealing,³⁷⁾ the expansion of lattice spacing may be caused directly by the introduction of defects. As discussed above in the case of paraffin crystals, however, the mode of surface affects the crystalline core, and then in the case of annealed single crystal whose mode of surface is analogous to that of mixed crystal of C_{32} and C_{35} , the expansion of (200) spacing may be due partly to the surface effects on the crystalline core.

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